

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Surface Treatment of Articles Composed of an Aluminium Base Alloy

- We, ALUMINUM COMPANY OF AMERICA, a corporation organised under the laws of the State of Pennsylvania, United States of America, of Alcoa Building, Pittsburg, Pennsylvania, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement: —
- This invention relates to the thermal treatment of articles of aluminium base alloys containing magnesium. More particularly, it is directed to a treatment for aluminium-magnesium alloys to prevent subsequent atmospheric and high-temperature oxidation and corrosion, and to facilitate degassing of finished and semi-finished articles of such alloys.
- Thermal treatments, such as preheating for hot-working, annealing, solution heat-treatment and aging, are generally employed during the fabrication of products from aluminium and aluminium base alloys. These treatments are usually carried out in air atmosphere furnaces. In an air atmosphere which has not been dried and at temperatures above 800° F. but below the melting point of the alloy, aluminium-magnesium alloy articles tend to blister and stain, resulting in an objectionable appearance and sometimes a considerable decrease in mechanical strength. This effect is referred to as high-temperature oxidation.
- Some finished and semi-finished articles of aluminium-magnesium alloys have been found to contain appreciable quantities of hydrogen, which may give rise to objectionable discontinuities in the metal structure. These discontinuities are generally quite easily detectable by ultrasonic testing techniques. It has been proposed to heat such articles in air for prolonged periods of time to diffuse hydrogen from the metal into the surrounding atmosphere. However, it has been found that the presence of small quantities of moisture in the surrounding atmosphere results in the failure of such degassing. This failure to degas may be explained by reaction between the metal surface and moisture forming metal oxides and a high hydrogen partial pressure at the metal surface which prevents loss of hydrogen from the metal into the surrounding atmosphere. In some cases, the hydrogen partial pressure may be sufficiently high to cause additional gassing of the metal.
- To minimize high temperature oxidation, various methods have been employed to protect these alloys at temperatures above 800° F. Specification 494,274 discloses the addition of fluorine-containing substances in vapour form to a non-dried air atmosphere to provide a protective environment or such alloys. The vapour is conveniently generated from solid compounds which decompose at the elevated temperatures, above about 800° F. The metal is usually charged to a furnace already heated to the desired high temperature and containing the protective atmosphere or supplied with the vapour-generating fluoride compounds if the protective atmosphere has not been previously provided, and it is quickly heated to the desired temperature.
- U.S. Patent 2,379,467 discloses a protective treatment for aluminium alloy forgings in which an aqueous solution of sodium fluoroborate is applied to the foregoing which is then dried prior to being heated to the solution heat treating temperature. The coated forging is quickly heated to the required temperature in accordance with conventional practice.
- Although these processes have been helpful in many cases, they have not eliminated altogether the undesirable blistering and staining which often occurs on articles of aluminium-magnesium alloys, nor have they

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proven effective in reducing the gas content of the metal.

It has been found that the blistering and staining of such alloys is apparently related to the oxidation of magnesium atoms at the external surface of the article and that the particles of these oxides or other oxy-compounds act as focal points or channels for further oxidation on and within the surface. This oxidation is apparently caused by the attack of water upon the surface, oxidizing the aluminium and magnesium and releasing hydrogen.

It has further been determined that above a certain critical temperature, there is a rapid increase in the rate of magnesium atom diffusion to the surface and concomitant oxidation of the magnesium. Whereas in previous methods oxidation has been inhibited by providing a protective atmosphere above that critical temperature, it has now been discovered that, for complete protection of aluminium-magnesium alloys they must be subjected to preliminary vapour treatment below that temperature, more particularly at a point below the onset of any substantial amount of magnesium oxidation.

It is an object of this invention to provide a preliminary thermal treatment for aluminium-magnesium alloy articles which substantially prevents high-temperature oxidation.

Another object is to provide a treatment for aluminium-magnesium alloy articles which will promote subsequent degassing of such articles in an atmosphere containing moisture.

It is also an object to provide a treatment for such articles which develops a surface condition that permits storage in industrial atmospheres for prolonged periods of time without corrosion.

A further object is to provide surface protection on aluminium-magnesium alloy articles which is stable at elevated temperatures in the presence of oxygen and moisture.

It has been found that the foregoing objects can be attained by a method of treating finished or semi-finished articles of aluminium base alloys containing magnesium wherein the articles are coated with an organic ammonium fluoroborate which yields boron trifluoride when heated to a temperature between 400° F. and 750° F., and heating the coated articles to a temperature between 400° F. and 750° F., but in all cases below the critical oxidation temperature of the alloy, for a period of time sufficiently long to cause substantial disappearance of the organic substance whereby a protective film is developed on the surface of the article which is substantially free from organic material. The alloy articles which have been treated in this manner strongly resist oxidation at temperatures above 800° F. and up to the melting point of the lowest melting point constituent in the alloy

which is often referred to as the temperature of incipient fusion. In addition the treated articles may be degassed by subsequent heating for prolonged periods of time, even in the presence of moisture.

The critical oxidation temperature of an aluminium-magnesium alloy is defined as the lowest temperature at which the formation of magnesium oxide can be detected by electron diffraction techniques. This may be a particular temperature or a very narrow temperature range on the order of 20° F., and hence the term is intended to cover both conditions. It is directly dependent upon the length of exposure in an untreated air atmosphere, the humidity of the furnace atmosphere, and the alloy composition, primarily the magnesium content. Although it can be determined readily for each set of conditions, it has been observed that these points fall within the range of 575 to 750° F., and generally 600 to 675° F.

Generally, the electron diffraction determination involves heating samples in air to various temperatures and under various conditions of humidity and time. After such treatment, the samples are exposed to an electron beam in diffraction apparatus wherein the beam is reflected from the surface of the samples and a pattern is made upon a film as in X-ray diffraction studies. By comparing the pattern with that of a known sample, the nature of the substance on the surface of the metal sample can be determined. This diffraction pattern provides a qualitative indication of the presence of magnesium oxide.

The term "aluminium-magnesium alloy" as herein employed refers to an aluminium base alloy containing on a weight basis 0.1 to 15 per cent magnesium, with or without the presence of other elements, such as from 0.1 to 12 per cent copper or 0.25 to 14 per cent silicon or 0.1 to 20 per cent zinc or 0.1 to 3 per cent manganese, or combinations of two or more of these elements. Any of the foregoing alloys may also contain one or more of the following elements, often referred to as "hardeners", in the following percentages:—

0.05	to 0.5 per cent chromium
0.01	to 0.5 per cent titanium
0.25	to 2.5 per cent nickel
0.01	to 0.5 per cent boron
0.002	to 2 per cent beryllium
0.1	to 0.5 per cent molybdenum
0.1	to 0.5 per cent zirconium
0.1	to 0.5 per cent tantalum
0.1	to 0.5 per cent columbium
0.1	to 0.5 per cent cobalt

However, the total amount of the latter elements should not exceed 3 per cent.

The term "aluminium base alloy" as used herein refers to those alloys which contain at least 50 per cent by weight of aluminium.

The term "organic boron trifluoride-carrier compound" as used herein refers to organic

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ammonium fluoroborates which yield boron trifluoride in a reactive state between 400 and 750° F. These compounds may be described as the products of reaction between fluoroboric acid, HBF_4 , and the constituent amine or amide. Generally, it is preferred to use compounds which decompose or yield boron trifluoride above 400° F. but below 575° F., the lowest critical oxidation temperature observed for an aluminium-magnesium alloy. The boron trifluoride, or substance containing boron trifluoride in a reactive state, is generally produced by the pyrolytic decomposition of the carrier compound. Compounds of this group may be used singly or in combination.

Examples of such carrier compounds are the aliphatic ammonium fluoroborates, di-n-butyl ammonium tetrafluoroborate, n-octadecyl N, N, N-trimethyl ammonium tetrafluoroborate, and di-n-amyl ammonium tetrafluoroborate.

It has been found that the boron trifluoride-carrier compounds should yield substantially no boron trifluoride below 400° F. since the protective film, if any, developed below this temperature is considerably less effective as an inhibitor than that produced by boron trifluoride above 400° F., possibly due to the formation of a different crystalline structure in the surface reaction product. Nevertheless, the carrier compound may decompose over a wide temperature range above 400° F. as is generally experienced in commercial products of this type which contain impurities. However, some decomposition may commence below 400° F., but the amount is small and can be disregarded.

The organic boron trifluoride-carrier compound is preferably applied to the surface of the aluminium-magnesium alloy in a solution, although it may be applied in a molten state. The solution may be applied by spraying, swabbing, or immersing the article. The preferred embodiment of this invention utilizes an alcoholic or aqueous solution of the organic boron trifluoride-carrier compound containing at least 0.4 per cent by weight of boron trifluoride and preferably about 2.6 per cent. In addition, wetting or other surface active agents may be added to improve the application. The coated articles are heated to a temperature of 400° F. or above where they are maintained until the organic substance substantially disappears and the fluoride film, which is substantially free from organic material, is formed. Periods from one to forty-five minutes have been satisfactory to accomplish this purpose. Treatment periods or less than one minute do not permit development of a satisfactory film or substantial disappearance of the organic coating while treatments in excess of forty-five minutes do not provide any additional protection or offer any further benefit. Generally, periods from one to twenty minutes are sufficient, however, longer times of

treatment are desirable in the case of alloys particularly susceptible to oxidation or when the surface oxide film is of greater thickness than that normally developed by exposure to the atmosphere.

The alloy articles treated in accordance with this invention may be subjected to higher heat-treating temperatures or may be removed for storage or subsequent heat treatment. The protective film developed effectively prevents atmospheric corrosion by industrial fume.

The present process may be practised in an untreated air atmosphere, i.e., a normal air atmosphere as commonly employed in heat-treating furnaces. No drying of the air need be undertaken as moisture can be tolerated; in fact, the invention has been successfully employed even in furnace atmospheres having dew points on the order of 125° F. Also, observations indicate that more satisfactory results are obtained when the furnace atmosphere contains at least $\frac{1}{4}$ grains of water per cubic foot or furnace volume, but it should not exceed 45 grains per cubic foot. In addition, the atmosphere may be contaminated with such substances as sulphur dioxide, hydrogen chloride, ammonia, carbon monoxide and carbon dioxide without adverse effect upon the action of the boron trifluoride.

Gases which are inert toward the aluminium-magnesium alloys may be employed in place of air such as nitrogen, argon, helium and fuel gas. The term "atmosphere" as used herein includes air, the inert gases, or combinations thereof.

Further, this invention is most effectively practiced when the alloy articles have not previously been subjected to temperatures above their critical oxidation temperature. The presence of magnesium oxide on the surface, which has been produced in preceding thermal treatments, is observed to reduce the effectiveness of boron trifluoride, presumably due to the formation of oxy-fluoride complexes, but there is still substantial benefit to be derived from the treatment of the present invention.

The temperature employed for the subsequent degassing treatment should be above 750° F. but below the temperature of incipient fusion of the alloy. As is well known, the higher the temperature, the greater the rate of diffusion and the shorter the time required. Generally, for aluminium-magnesium alloys a temperature of 900 to 975° F. has been found satisfactory.

The period for the degassing treatment will depend primarily on the thickness of the article being treated (the shortest diffusing path). Generally at 940° F. periods in excess of several hours and up to 20 days or more are necessary; for articles having a maximum cross-section of $\frac{1}{2}$ inch, periods in excess of 16 hours have been found adequate. A thickness of 1 inch will generally require a period in excess of 40 hours at the same temperature;

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10 to 15 days may be required for cross-sections. i.e. thicknesses, larger than 3 to 4 inches. Generally, the time required for the treatment will be related to the rate of hydrogen diffusion in the alloy at a given temperature.

Subsequent to the degassing treatment, the treated article should be subjected to a working step to effect some reduction in size, thus healing the voids left by the diffused hydrogen. The percentage of reduction necessary will be determined by the nature of the article and its original gaseous content.

The term "degassing" as used herein, contemplates both the removal of gas from the metal and the prevention of regassing of the metal.

The efficacy of the present invention is illustrated by the following examples:—

EXAMPLE 1.

A lot of 0.01 inch foil test strips of an alloy consisting of aluminium, 1.5 per cent magnesium, 4.5 per cent copper and 0.65 per cent manganese was divided into two groups of specimens and heat treated for 16 hours at 920° F. in an air atmosphere having a dew point of 125° F. The first group of specimens had been pretreated by swabbing with a solution containing 7.5 per cent by weight of di-n-butyl ammonium tetrafluoroborate in isopropyl alcohol and heated to a temperature of 500 to 550° F. for a period of five minutes. Upon the removal from the heat-treating operation, the first group of specimens was found to be free from blistering and staining but the untreated group was moderately blistered and had a grey-black stain.

EXAMPLE 2.

A lot of 0.01 inch foil test strips of an alloy consisting of aluminium, 2.5 per cent magnesium and 0.25 per cent chromium was divided into two groups of specimens and heated 16 hours at a temperature of 950° F. in an air atmosphere having a dew point of 125° F. The first group of specimens had been pretreated by swabbing with a solution containing 10 per cent by weight of n-octadecyl N,N,N-trimethyl ammonium tetrafluoroborate in isopropyl alcohol and heated to a temperature of 550° F. for a period of ten minutes. Upon examination the pretreated group of specimens was found to be free from blistering and staining while the untreated was moderately blistered and had a dark grey stain.

EXAMPLE 3.

A lot of 0.01 inch foil test strips of an alloy consisting of aluminium, 1.0 per cent magnesium and 0.3 per cent manganese was divided into two groups of specimens and heated for 16 hours at a temperature of 950° F. in an air atmosphere having a dew point of 125° F. The first group of specimens had

been pretreated by swabbing with a solution containing 7 per cent by weight of di-n-amyl ammonium tetra-fluoroborate in isopropyl alcohol and heated to a temperature of 575° F. for a few minutes. Upon inspection the pretreated group was free from blistering and staining but the untreated was moderately blistered and had a grey-black stain.

EXAMPLE 4.

A lot of sheet ingots of an alloy consisting of aluminium, 2.5 per cent magnesium, and 0.25 per cent chromium was divided into two groups of specimens and preheated for 30 hours at a temperature of 950° F. prior to hot-rolling into sheet. The first group had been pretreated by swabbing with a solution of 7.5 per cent by weight of di-n-butyl ammonium tetrafluoroborate in isopropyl alcohol and heated through a temperature range of 450 to 575° F. for a period of thirty minutes. Upon inspection after preheating, the pretreated ingots were found to be free from staining although the untreated had a grey-black to blue-black stain indicating heavy oxidation.

EXAMPLE 5.

At lot of $\frac{1}{2}$ inch thick specimens was taken from a forging ingot of an alloy nominally consisting of aluminium, 4.4 per cent copper, 0.9 per cent silicon, 0.8 per cent manganese and 0.4 per cent magnesium. The ingot had been rejected because of porosity. The specimens were divided into two groups and heated at 950° F. for 16 hours in an air atmosphere having a dew point of about 80° F. One group of specimens was pretreated by swabbing with a solution containing $7\frac{1}{2}$ per cent by weight of di-n-butylammonium tetrafluoroborate in isopropyl alcohol and heated at a temperature of 450 to 550° F. for about 15 minutes. The other group received no preliminary treatment. Upon removal from the furnace, both groups of specimens were subjected to gas evaluation by rapidly heating the specimens under reduced pressure to magnify voids. Upon inspection, the treated group of specimens was found to be free from such magnified voids whereas the untreated showed moderate to considerable quantities of such magnified voids. This test indicates that the treatment of the present invention enabled the degassing of even rejected metal by heating for extended periods of time in an atmosphere containing moisture.

WHAT WE CLAIM IS:—

1. A method of treating a finished or semi-finished article composed of an aluminium base alloy containing from 0.1 to 15 per cent magnesium, which comprises coating said article with an organic ammonium fluoroborate which yields BF_3 when heated to a temperature between 400° F. and 750° F., and heating said coated article to a temperature between

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- 400 and 750° F. but below the critical oxidation temperature of said alloy for a period of time sufficiently long to cause substantial disappearance of the organic ammonium fluoroborate.
- 5 2. A method according to Claim 1, in which the organic ammonium fluoroborate comprises di-n-butyl ammonium tetrafluoroborate, n-octadecyl-N,N,N-trimethyl ammonium tetrafluoroborate, or di-n-amyl ammonium tetrafluoroborate.
- 10 3. A method according to Claim 1 or 2, in which the organic ammonium fluoroborate yields BF₃ when heated to a temperature between 400° F. and 575° F., and said coated article is heated to a temperature between 400 and 575° F.
- 15 4. A method according to any of Claims 1 to 3, in which said coated article is heated in an air atmosphere.
- 20 5. A method according to Claim 4, in which the air atmosphere contains at least $\frac{1}{4}$ but not more than 45 grains of water per cubic foot.
6. A method according to any of Claims 1 to 5, in which said article is subsequently degassed by thermal treatment at a temperature above 750° F. but below the temperature of incipient fusion.
- 25 7. A method of treating a finished or semi-finished aluminium base alloy article substantially as hereinbefore described with reference to the examples.
- 30 8. A finished or semi-finished article composed of an aluminium base alloy containing from 0.1 to 15 per cent magnesium when treated by the method according to any of Claims 1 to 7.
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STEVENS, LANGNER, PARRY
& ROLLINSON,
Chartered Patent Agents,
Agents for the Applicants.

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